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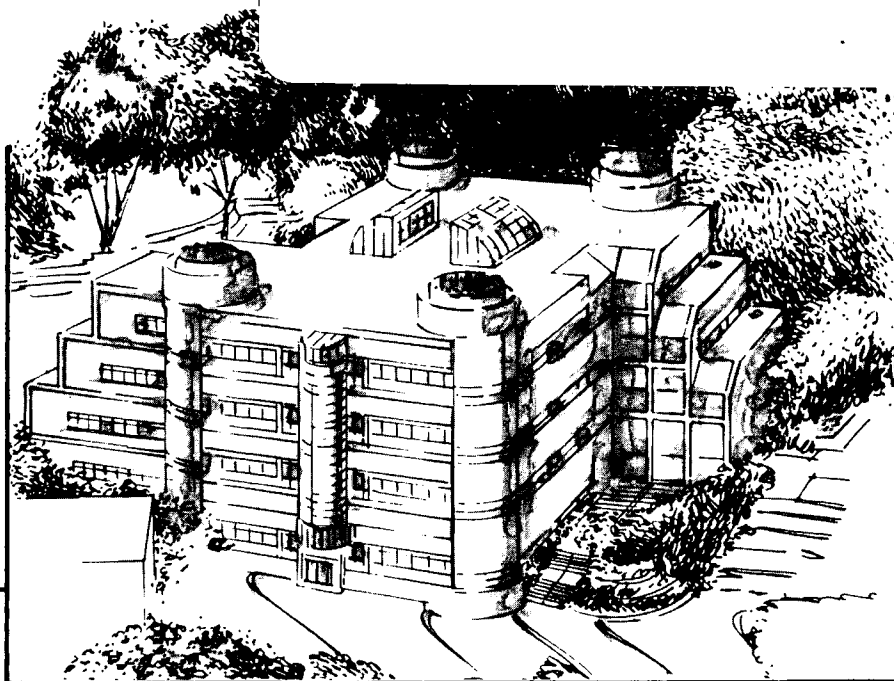
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Superconductivity in Ceramic Materials**

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Abstract

A mechanism of superconductivity of ceramic compounds caused by a Bose condensation of lone singlet s^2 electron pairs is proposed. The mechanism is applied to a situation when an "electrically active" element with the s^2p^{n-1} outer electron structure, like $Tl(s^2p)$, $Pb(s^2p^2)$, $Bi(s^2p^3)$, substitutes a $+n$ valence atom contributing n electrons to a covalent bonding. Since lone electron pairs usually cannot be split, the atoms with the s^2p^{n-1} structure are transformed into a mixture of atoms in the (s^2p^0) and (s^0p^0) valence states according to the $2A^{n+} \rightarrow A^{(n+1)+} + A^{(n-1)+}$ reaction. A spatial distribution of atoms in two valence states is equivalent to the distribution of lone electron pairs over A atom sites. The superconductivity is expected when a band formed by tunneling of the pairs is within a conduction or valence band so that concentration of the pairs can be reduced to a small value and the Bose condensation of real space-localized pairs may occur. The proposed mechanism is an alternative to the BCS mechanism of weakly bonded pairs. It predicts the linear dependence of the specific heat on temperature at the superconducting state, and weak if any isotope effect. The $PbTe:Tl$, $Ba(Pb,Bi)O_3$ and $InTe$ examples of the lone pair superconductivity are considered. The possible extension of the lone electron pair concept to the high temperature superconductors like $YBa_2Cu_3O_7$ with "electrically active" transitional element atoms with mixed valences differing by two is discussed.

The recent discovery of high-temperature superconductivity in Cu oxides^[1, 2] generated the great interest in this class of materials. There is a growing feeling that the superconductivity mechanism in these ceramic systems may be somehow different from the conventional phonon-mediated BCS mechanism. Because great efforts are directed now at Y-Ba-Cu and La-Ba-Cu oxides, the importance of some other simpler ceramic superconductors which may shed light on the mechanism of high-temperature superconductivity is largely overlooked. Good examples of such superconductors are the PbTe hole IV-VI semiconductor compound doped by Tl with the superconducting temperature $T_c \approx 1.3$ K discovered by Chernik and Lykov in 1981^[3], and $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ perovskite structure oxide with $T_c \approx 13$ K discovered by Sleight et.al. in 1975^[4]. These compounds display physical properties which, we believe, make them important for understanding certain aspects of high-temperature superconductivity and may give a lead in searching for new hi- T_c materials. The electron pairing mechanism resulting in superconductivity in these compounds presumably is not the BCS phonon-mediated mechanism. Unlike the later one, it is associated with intraatomic electron-electron correlations rather than with effects introduced by the presence of other atoms. This kind of pairing which is discussed below may explain some unusual features of the ceramic superconductors.

As is well known from inorganic chemistry, certain nontransitional heavy elements may have two valence state differing by 2. This situation usually occurs for elements whose s^2p , s^2p^2 , s^2p^3 outer electrons may participate in covalent binding. This valency exclusion rule is associated with the fact that intraatomic electron correlations do not allow splitting s^2 singlet electron pair so that only one s electron (together with p-electrons) would be contributed to the covalent binding. An atom either contributes an entire s^2 electron pair or does not contribute it at all. This circumstance is the basis for a lone or inert electron pair concept^[5] widely used in solid state chemistry.

Let us consider a heavy impurity A atom with the electronic structure s^2p^{n-1} where $n = 2, 3, 4, 5$. This atom may have two possible valences, $A^{(n-1)+}$ (s^2p^0) and $A^{(n+1)+}$ (s^0p^0). If an A atom substitutes a host lattice atom which must contribute n electrons to the covalent binding, it results in



reaction. $A^{(n-1)+}$ atoms in the (s^2p^0) valence state have s^2 singlet lone electron pairs on them while the remaining A atoms in the $A^{(n+1)+}$ valence state have none.

The lone electron pair formation on a site may be formally described in terms of a negative U center model, assuming electron-electron attraction U ($U < 0$) on a site equal to the dissociation energy of the pair. Each A atom which hosts a lone electron pair can be regarded as a so-called negative U center. A system PbTe:Tl is a good example. Any

Tl (s^2p) impurity atom can exist only in the two valence states, Tl^+ (s^2p^0) and Tl^{3+} (s^0p^0) [$A = Tl$, $n = 2$]. Tl atom placed in a valence +2 position of a Pb host atom transforms according to $2Tl^{2+} \rightarrow Tl^+ + Tl^{3+}$ reaction (1). The same occurs when Bi (s^2p^3) atoms are placed in a position of Pb in $Ba(Pb_{1-x}Bi_x)O_3$ requiring the valency +4. Then $Bi^{4+} \rightarrow Bi^{5+} + Bi^{3+}$ reaction takes place. In both cases there is the one electron on a site situation. In this situation electrons (or their holes) aggregate into lone electron (hole) pair gas. The above described mechanism of a negative U-center formation is, in fact, associated with properties of a single A atom. This makes it substantially different from the multiatomic Anderson relaxation mechanism^[6].

A lone electron pair may tunnel into a nearest-neighbor site. It transforms the negative U level related to a pair into a narrow band. The tunneling occurs due to a virtual process, splitting the pair and hopping both its electrons to the nearest site. This process gives the bandwidth of the pair (its efficient hopping integral) to be of the order of $\frac{t^2}{U}$ where t is the hopping integral of a single electron. A singlet lone electron pair may be regarded as a Bose quasiparticle. This assumption is, however, valid as long as the obviously non-Bose exclusion rule (following from the Pauli principle that two-electron pairs cannot occupy the same site) can be neglected. The neglect is justified when the number of pairs per site, v , is a small number. The gas of such Bose quasiparticles may undergo the Bose condensation at low temperature resulting in superconductivity. At high density of pairs ($v \approx 1/2$) when they cannot be regarded as Bose quasiparticles anymore, the superconducting state is destroyed. It occurs due to the real space long-range ordering of pairs. The pair ordering may be perceived as an ordered distribution of A atoms in two valence states, $A^{(n+1)+}$ and $A^{(n-1)+}$. This type of ordering, similar to so-called Verwey ordering observed in the mixed valence materials like magnetite^[7] and V_nO_{2n-1} ^[8], is visualized due to atomic relaxation making A atoms crystallographically nonequivalent.

The concept of a lone electron pair localized on a lattice site is applicable to the situation when the kinetic energy increase caused by spatial localization of two electrons on a site is outweighed by the attractive negative U interaction on the site, i.e., in the narrow band width case when $\frac{t^2}{U} \ll 1$. In the case discussed above, the narrow band (or energy level) is introduced by impurity atoms A with mixed valencies. If the impurity band proves to be within the energy gap, the reaction (1) gives 50:50 ratio of $A^{(n-1)+}$ and $A^{(n+1)+}$ atoms. The impurity level pins the Fermi level, E_F , upon a doping because any introduced charge carriers just shift the balance between $A^{(n+1)+}$ and $A^{(n-1)+}$ states. This is the case with $PbTe:In$ ^[9]. The other two possible and most interesting cases are related to a more complicated situation when the impurity level related to lone electron pairs proves to be either within a conduction band (like $PbTe:Ga$ ^[9]) or within a valence band (like $PbTe:Tl$ ^[9]). Then the distance from the bottom of the conduction band to the impurity level determines the number of lone electron pairs. In this situation the number of lone electron pairs can be controlled by doping. This is a band interpretation of the reaction (1). It is noteworthy that the relevant system is characterized by the coexistence of two systems, the conventional Fermi gas of electrons and the gas of electron pairs, the situation which does not take place for BCS superconductors. The case when the impurity level proves to be in the valence band is similar. The only difference is that the role of electrons and their pairs is played by holes and their pairs. The simplest adequate model of a system with local electron

pairs (like lone s^2 electron pairs) in the ground state is the Hubbard model with negative U interaction providing formation of electron pairs. The real space localization of pairs in the negative U model depends on the $t/|U|$ ratio. The pairs are completely localized on sites at $\frac{t}{|U|} \ll 1$ (narrow band and large electron-electron attraction on a site). They may be of the order of several interatomic distances at $\frac{t}{|U|} \approx 1$ and they are delocalized at $\frac{t}{|U|} \gg 1$ (the BCS case). The theory based on the Hubbard model with negative U centers in the $\frac{t}{|U|} \gg 1$ limit was proposed by Emery [10] and Kulik and Pudan [11] long time before the discovery of the high- T_c superconductivity. It gives the same picture of the Bose condensation of localized pairs as described above. According to [11] in the mean field approximation (unlike the delocalized pair case it is not a very good approximation here) the Bose condensation of local electron pairs occurs at the transition temperature given by:

$$T_c = W (1-2v) \left[\ln \frac{1-v}{v} \right]^{-1} \quad (2)$$

where v is the number of electron pairs per lattice site, $W \approx \frac{t^2}{|U|}$ is a bandwidth related to the hopping of a pair. It follows from (2) that: (i) superconduction transition is not affected directly by the phonon spectrum and thus does not display the considerable isotope and phonon softening effects: (ii) the superconducting temperature, T_c , is determined by the bandwidth, W , and thus there is no reason why it could not be high. The other conclusion is the formation of a long-range ordering of pairs at the high density, v , limit. The lone electron pair mechanism of superconductivity described above is in agreement with the observation results for PbTe:Tl and Ba(Pb,Bi)O_3 .

PbTe:Tl. It is well-established that the superconductivity in PbTe:Tl is determined by Tl resonant impurity states in the valence band [3,12]. The Ginzburg - Landau parameter K is found to be 95, close to about 100 for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [13], commensurate with ≈ 20 for Ba-La-Cu oxide and is huge with respect to conventional metal superconductors. It was found that in spite of considerable TO phonon softening induced by Ge impurity which was observed in the specific heat measurements, the sharp decrease in T_c occurs [14]. This is just the opposite of what would be expected from the BCS phonon-mediated mechanism. But all these results can be understood in terms of the lone electron pair mechanism proposed above. Indeed, in this case part of Tl atoms in the valence state +1 have a lone pair on them whereas the other part in the valence state +3 have none (i.e., have a lone hole pair). The fraction of lone hole pairs $v = \text{Tl}^{3+}/(\text{Tl}^{+} + \text{Tl}^{3+})$, depends on the depth of impurity level with respect to the top of the valence band. These real space singlet pairs can be regarded as Bose quasiparticles whose condensation into the superfluid state provides superconductivity. This mechanism is not directly affected by the electron-phonon interaction and, therefore, may not be considerably dependent on the phonon softening. Increase of T_c upon increase of the number of holes observed in [14] is also in agreement with the local pair condensation concept because it is predicted by eq (2).

$\text{Ba(Pb}_{1-x}\text{Bi}_x)\text{O}_3$. This remarkable example of superconductivity in a ceramic compound (which possibly was a lead to the discovery of high- T_c superconductivity in copper oxides) was found by Sleight et al [4]. Maximum superconductivity occurs at

$T_c \approx 13\text{K}$ at $x \approx 0.25$. Superconductivity exists up to $x \approx 0.35$. Bi atoms occupy the Pb atom sites in the BaPbO_3 perovskite lattice which requires the valence state to be +4. As was discussed before, Bi atoms in such a case should dissociate into Bi^{3+} (s^2p^0) and Bi^{5+} (s^0p^0). The Bi^{3+} atoms have a lone electron pair on them. If we assume the band scheme proposed in [4] and that the Bi resonant impurity band is in the conduction or valence band, the fraction v of lone electron pairs (fraction of Bi^{3+} atoms) is determined by the position of the impurity level with respect to the bottom of a conduction or the top of a valence band. The lone electron pairs at the low concentration limit may undergo the Bose condensation resulting in superconductivity.

Hall effect measurements at 77 K have shown that the number of charge carriers takes its maximum value at $x \approx 0.25$ and drops to zero around $x \approx 0.35$. The maximum of T_c is also observed at the same Bi content as the maximum of charge carriers. Similar to the PbTe:Ti case, the carrier concentration and T_c show the similar dependence on x [15]. These observations apparently agree with the lone electron pair condensation mechanism if we assume that part of the carriers exists in the form of lone electron pairs and the T_c versus v dependence can be at least qualitatively correctly described by eq (2). The observed transition from the superconducting field to the semiconducting field of the T - x diagram at $x \approx 0.4$ also directly follows from the real space pair model and does not require any other additional arguments unrelated to the model. It is just the transition from the superfluid state to the spatial long range ordering of pairs which is predicted by the real space pair model when $v \approx 1/2$ and was discussed above. The real space ordering of pairs interpreted as ordering of Bi^{3+} and Bi^{5+} atoms was really observed near the BaBiO_3 stoichiometry. The GL constant for Ba(Pb,Bi)O_3 superconductor is about 80 [16] which is close to 90 observed for PbTe:Ti and 100 estimated for $\text{YBa}_2\text{Cu}_3\text{O}_7$ [13].

Discussion

To our knowledge, Sleight was the first who made the very important observation that "disproportionation" reaction of the type (1) of a mixed valence element may somehow play the key role in superconductivity of ceramic oxides [17]. The lone electron pair mechanism discussed above shows how the chemical concept of disproportionation may work here. The proposed model of Bose condensation of lone electron pairs (or hole pairs) is in good agreement with more simple and well studied PbTe:Ti systems, and, we believe, give reasonably good explanation of the effects observed in $\text{Ba(Pb}_{1-x}\text{Bi}_x\text{)O}_3$. It should be mentioned that the Bose condensation gives a gapless superconductivity. It is, however, approximately true as long as $v \ll 1$ when the real space local electron pairs can be regarded as Bose quasiparticles. At larger v when the Pauli principle forbidding two pairs to be at the same site cannot be ignored, the excitation spectrum of the superfluid condensate should have a gap. The simplest negative U Hubbard model gives $\Delta(0) = Wv$ at $v \ll 1$ and $T=0$ K where $\Delta(0)$ is the gap [11]. Therefore, the superconducting state is almost gapless at $v \rightarrow 0$ and has an appreciable gap at the higher v . It should be emphasized that the $v \ll 1$ condition imposes the severe constraint on the concentration of carriers in the superconducting state and thus potentially could be the cause of the problem of a critical current.

One of the consequences of the model is that it does not predict dependence of superconductivity on the density of states on the Fermi level. The other consequence is that it predicts the unusual behaviour of the specific heat in the superconducting state. Indeed, in the relevant cases when the negative U band is within the conduction (or valence) band, there is the coexistence of the Fermi liquid formed by single particle charge carriers (electrons or holes) and the superfluid liquid of pairs. It would mean coexistence of the superconducting and nonsuperconducting component of the electronic gas (it somehow reminds the coexistence of superfluid and nonsuperfluid components in liquid He). Such a two-component system is superconducting but its specific heat should also have two components: the electronic one, γT , and exponential one proportional to $\exp(-\frac{\Delta}{T})$ where Δ is the gap. This situation definitely cannot occur in a BCS superconductor. We do not know whether these specific heat abnormalities are observed in PbTe:Ti or Ba(Pb,Bi)O₃ but the linear term in the temperature dependence of the specific heat was observed in Y - Ba - Cu oxide [18, 19].

Intraatomic correlation producing a lone electron pair is not the only possible mechanism which may be treated in terms of a negative U center model. The strong electron-phonon interaction in the narrow band case may result in localization of electrons in the polaron states, and in some cases formation of bipolarons [20] when the energy gain associated with the local lattice relaxation overweighs the Coulomb repulsion [6,21]. This is just another mechanism of the negative U center formation. It would also lead to the Bose condensation of pairs [20]. The mechanism may be substantial for mixed valency transitional elements in material with a soft phonon mode.

The third mechanism of formation of localized pairs could be associated with the geometry of ligands surrounding an "active" atom with mixed valency. The field of the ligands may destabilize the average valency of the mixed valency atom required by the chemical bonds. In this situation the "disproportionation" reaction (1) occurs. For example, there are two types of coordination polyhedrons for Cu atoms in the YBa₂Cu₃O₇ compound, the square around Cu(III) and the pentagonal polyhedron (pyramid) around Cu (II). The average valency of Cu (II) atoms in YBa₂Cu₃O₇ is + 2. Since Cu²⁺ atoms usually require the octahedral coordination [5], the valence state +2 could be unstable in the five-fold coordination resulting in the reaction (1), $2 \text{Cu}^{2+} \rightarrow \text{Cu}^{+} + \text{Cu}^{3+}$. If it is really the case, the situation similar to that in PbTe:Ti and Ba(Pb,Bi)O₃ would occur, and the Bose condensation of electron pairs localized on Cu⁺ atoms might be expected. This would explain the high-T_c superconductivity, absence or small value of the isotope effect and the linear dependence of the specific heat on the temperature in the superconducting state. This would also result in predicting the superconductivity over Cu (II) atoms in the (001) planes nearest to Y atoms.

The proposed mechanism of superconductivity based on formation of two valence states differing by two gives a certain lead to searching for the prospective materials. The main idea is to choose a mixed valency alloying element which may have at least two valence states different by 2 and introduce it into sites of the compound requiring the valencies intermediate between the permitted ones (like Ti⁺ and Ti³⁺ placed in a position of Pb²⁺).

The other lead is to look for compounds where ordered distribution of atoms in different valence states different by 2 really occurs (like $\text{Ba}(\text{Bi}^{3+})_{1/2}(\text{Bi}^{5+})_{1/2}\text{O}_3$).

In the specific case of BaBiO_3 $v = \frac{\text{Bi}^{3+}}{\text{Bi}^{3+} + \text{Bi}^{5+}} = \frac{1}{2}$, i.e., it is out of the Bose condensation range. If, however, we manage to find an alloying element which would shift the negative U level into the conduction (or valence) band, then the concentration of pairs, v , may be reduced to the level where the Bose condensation occurred. This is presumably realized for Ba Bi O_3 alloyed by Pb.

After finishing this paper we tried to find several prospective systems which would meet the above-discussed requirements. One of them was found at once. It is the InTe compound with 696°C melting point. The In atoms have two nonequivalent positions in the crystal lattice, corresponding to two valence state $\text{In}^+(s^2p^0)$ and $\text{In}^{3+}(s^0p^0)$. The reported metallic conductivity instead of semiconductivity is consistent with the assumption that the impurity level related to electron (hole) pairs is within a conduction or valence band. Leaking of electrons (holes) from the impurity lone s^2 pairs band to the conduction (valence) band may reduce the concentration of pairs, v , to the level where the Bose condensation could be expected. It is of great interest that comparatively high temperature superconductivity at 10 K was reported for this system^[22].

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